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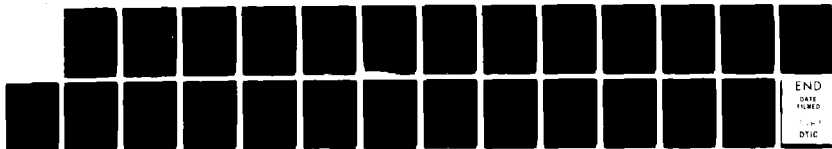
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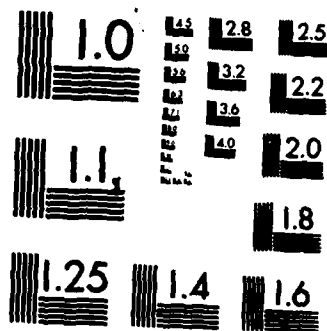
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Magic Angle Spinning NMR of Conducting Polymers

by

T. C. Clarke, J. C. Scott, and G. B. Street

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# Research Report

MAGIC ANGLE SPINNING NMR OF CONDUCTING POLYMERS

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## MAGIC ANGLE SPINNING NMR OF CONDUCTING POLYMERS

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**ABSTRACT:** Because of their typically intractable nature, conducting polymers as a class of materials have proved particularly difficult to characterize by the conventional techniques of polymer analysis. We present here examples of the application of a powerful new tool, cross-polarization magic angle spinning (CPMAS)  $^{13}\text{C}$  NMR spectroscopy, to the investigation of the structure and reactions of the conducting polymers polyacetylene and polypyrrole. ←

*(revised 1/14/83)*

(13)

## INTRODUCTION

Although the emerging class of conducting organic polymers<sup>1</sup> represents a unique opportunity to blend traditional polymer materials properties with interesting new electronic properties, the investigation of these materials has been limited somewhat by the difficult characterization problem they present. In their conducting form all of these polymers are essentially intractable, exhibiting no melting point or glass transition temperature and no solubility. Thus, many of the more common polymer characterization techniques are inapplicable in the study of conducting polymers. Fortunately, the development of new analytical tools continues to provide new approaches to characterization. In particular one relatively recent spectroscopic technique, cross-polarization magic angle spinning (CPMAS)  $^{13}\text{C}$  NMR,<sup>2</sup> has proved extremely useful in providing new insights into the structure and reactions of these materials.

Prior to 1975,<sup>3</sup> high resolution NMR spectroscopy was limited essentially to samples in solution. Conventional NMR on solids yields extremely broad spectra, primarily because of the large magnitude of the  $^{13}\text{C}$ - $^1\text{H}$  dipolar interaction, typically 10-40 kHz. ( $^{13}\text{C}$ - $^{13}\text{C}$  interactions are relatively unimportant because the natural abundance of this isotope is only 1.1%.) The  $^{13}\text{C}$ - $^1\text{H}$  dipolar coupling can be removed by high power decoupling, leaving the carbon chemical shift anisotropy as the dominant broadening mechanism. In the NMR experiment the local magnetic field at a given carbon is a function of the relative molecular orientation with respect to the external magnetic field. Thus, the observed spectrum for a typical solid would represent a superposition of all possible molecular orientations, as opposed to spectra obtained on liquids where rapid tumbling of the molecules leads to observation of an average (isotropic) chemical shift. However, careful analysis reveals that this broadening can be removed by spinning the solid sample at a rate rapid compared to the

anisotropy (expressed in frequency units) about an axis inclined at an angle of  $54.7^\circ$  (the "magic angle") with respect to the external field. This process leads to an averaging of the anisotropy and results in a single narrowed absorption at a position characteristic of the isotropic chemical shift.

The sensitivity of  $^{13}\text{C}$  NMR spectroscopy is normally limited by the low natural abundance of the magnetic isotope and its small magnetic moment and long relaxation time. The situation can be improved, however, by the use of cross polarization (CP). Using an appropriate pulse sequence, polarization can be transferred from the protons to the carbons, resulting in a significant enhancement in carbon magnetization over the normal value. Moreover, CP allows successive free induction decays to be obtained on the time scale of the proton spin-lattice relaxation time rather than on the longer time scale of the carbon spin-lattice relaxation time, resulting in more rapid acquisition of the carbon spectrum. Together cross polarization and the magic angle spinning procedure allow one to obtain high resolution spectra of solids, a technique which we have found to be invaluable in the analysis of conducting polymers.

## POLYACETYLENE

In many respects polyacetylene,  $(\text{CH})_x$ , is the simplest of the conducting polymers. First synthesized as an insoluble black powder in 1956 by the polymerization of acetylene,<sup>4</sup> polyacetylene attracted only sporadic attention until 1971, when Shirakawa developed a technique for the growth of shiny, flexible films of this material on the surface of a Ziegler-Natta catalyst solution.<sup>5</sup> Coupled with this synthetic advance, the discovery in 1977 that the conductivity of polyacetylene could be raised from its normal value of  $10^{-10} \text{ ohm}^{-1}\text{-cm}^{-1}$  to greater than  $10^3 \text{ ohm}^{-1}\text{-cm}^{-1}$  by treatment with oxidizing or reducing agents has led to the current intense interest in this material and its analogs.<sup>6</sup>

Polyacetylene is typically synthesized as the *cis-transoid* isomer (Ia) but can be converted to the thermodynamically more stable *trans-transoid* (Ib) form by heating. The normal solid state  $^{13}\text{C}$  NMR spectra of the individual isomers are essentially identical broad featureless absorptions. As first shown by Maricq *et al.*,<sup>7</sup> however, application of CPMAS  $^{13}\text{C}$  NMR (with proton decoupling) provides sharp well separated peaks for the *cis* and *trans* isomers at positions comparable to those observed in model compounds (Fig. 1). Subsequently, Kaplan and coworkers have used CPMAS  $^{13}\text{C}$  NMR in a detailed examination of the *cis-trans* isomerization process.<sup>8</sup> However, it is in the study of the doping of polyacetylene that CPMAS  $^{13}\text{C}$  NMR has provided the most unique insights.<sup>9</sup>

The nature of the semiconductor-to-metal transition which occurs in polyacetylene at doping levels of  $\sim 1\%$  has been the source of considerable controversy. On the basis of a linear increase in Pauli susceptibility with increasing dopant concentration, Tomkiewicz *et al.* proposed a model of inhomogeneous doping, leading to the formation of metallic islands which grow in size and/or number as doping progresses.<sup>10</sup> In this picture, the semiconductor-to-metal transition corresponds to a percolation threshold. On the other hand, Heeger and coworkers have claimed that slower doping leads to a more homogeneous dopant distribution, which allows the proposed soliton nature of polyacetylene doping to be observed.<sup>11</sup> Heeger's susceptibility measurements support the model of a metallic state with spinless carriers (charged solitons) in the 1 to 7% doping regime.

In an attempt to resolve this problem Peo *et al.* examined the solid state  $^{13}\text{C}$  NMR spectrum of polyacetylene at various  $\text{AsF}_5$  doping levels using magic angle spinning.<sup>12</sup> In studying only *cis*-polyacetylene, they reported no substantial change in the  $^{13}\text{C}$  spectrum up to doping levels of  $\sim 7\%$   $\text{AsF}_5$ , at which point a rather abrupt change to a broad, shifted line was observed. These authors attributed the change to a Knight shift and correlated this



result with the sudden increase in Pauli susceptibility in Heeger's measurements at ~7% doping (attributed to overlap of the soliton band with the valence and conduction bands).<sup>11</sup> However, several puzzling aspects of the Peo data led us to extend their study. Particularly disturbing was their failure to observe even a chemical shift in the polyacetylene at doping levels below 7%, despite the fact that doping is believed to remove charge from the polymer  $\pi$ -system.

Polyacetylene for our experiments was prepared by the procedure of Ito *et al.*<sup>5</sup> Conversion of *cis*-polyacetylene to the *trans* isomer was carried out under ~0.5 atm of helium at 200°C for one hour. The AsF<sub>5</sub> was purified as described earlier.<sup>13</sup> Doping of the polyacetylene was performed as described in the work of Ikehata *et al.*<sup>11</sup> Final compositions were determined by weight uptake. All manipulations of the polymer were carried out either on a vacuum line or in an inert atmosphere dry box. In particular the NMR sample rotors were loaded in the dry box and transferred to the spectrometer under argon. Undoped samples were cut into small pieces before being packed in the rotors; doped samples were cut and dispersed by grinding with glass powder before loading. An undoped *cis* sample was also cut and ground to ensure that no sample degradation or *cis-trans* isomerization occurred on grinding. During the acquisition of data the sealed rotors were under a constant flow of helium. Spectra were obtained in a magnetic field of 15 kOe using cross polarization and magic angle spinning techniques. Shifts are expressed in ppm with respect to tetra-methylsilane (TMS).

Figure 2 shows our results for the doping of *cis*-CH<sub>x</sub>. The bottom spectrum is that of the undoped starting material. The main peak at 127 ppm corresponds to *cis* material; the low-field shoulder (~136 ppm) is due to the presence of a small amount of the *trans* isomer.<sup>7,8,12</sup> The top spectrum shows the same material after doping to a composition of

(CH(AsF<sub>6</sub>)<sub>0.068</sub>). As in the Peo data<sup>12</sup> a very broad resonance centered at ~150 ppm is observed. The origin of this downfield shift in the doped polymer is discussed in detail below.

The middle spectrum in Figure 2 shows a *cis* sample doped to the intermediate concentration of 3 mole %. Superficially, this spectrum resembles those presented by Peo *et al.* for intermediate doping levels: a sharp and apparently unchanged *cis* line as well as a slightly larger *trans* shoulder are readily evident. However, in contrast to the Peo results, we find that these peaks lie on top of a rather broad peak shifted downfield to a position characteristic of the doped polymer. This feature is more apparent in the expanded spectrum of the 3% sample shown in Fig. 3. This broad peak, smaller in relative intensity, is also found in a 1% doped *cis* sample (Fig. 4).

Figure 5 shows comparable data for AsF<sub>5</sub> doped *trans*-CH<sub>x</sub>. (For experimental reasons only, a 5% lower limit on the composition of the heavily doped sample could be determined.) The heavily doped sample exhibits a spectrum quite similar to that of 7% AsF<sub>5</sub> doped *cis*-polyacetylene. However, the spectrum of the 3.2% *trans* sample is quite dramatically changed from that of the undoped *trans* material, and appears to consist of a somewhat broadened peak at the original *trans* position lying on top of the broader downfield signal characteristic of the heavily doped material.

From these data we draw several conclusions: (1) Low levels of doping do not lead to extensive conversion of *cis*-polyacetylene to the unoxidized *trans* isomer. (2) In contrast to the results of Peo *et al.*, however, signals characteristic of the doped polymer can be seen in the spectrum of AsF<sub>5</sub> treated *cis*-polyacetylene at doping levels as low as 1%. Whether these signals correspond to material which is *cis* or *trans* in nature cannot be answered

directly by these experiments; the observation of very similar spectra for heavily doped *cis* and *trans* material is consistent with previous suggestions that the doped material is very likely *trans*.<sup>14</sup> (3) In the first  $^{13}\text{C}$  NMR examination of  $\text{AsF}_5$  doped *trans*- $\text{CH}_x$ , we find that 3% doping causes a distinct broadening of the original *trans* line as well as the onset of the broad downfield signal centered at  $\sim 150$  ppm. In contrast, the spectrum of a 3% doped *cis* sample looks essentially like a superposition of the signals of undoped *cis* and heavily doped *cis*. Together these results suggest that the doping of *cis*- $\text{CH}_x$  is considerably less uniform than that of *trans*- $\text{CH}_x$ . Even the *trans* doping, however, does not appear to be completely uniform.

The downfield shift in the doped polyacetylene has been explained as a Knight shift.<sup>12</sup> However, the position of this signal is comparable to the shifts observed for the carbons of delocalized  $\pi$ -carbonium ions where no conduction electrons are present. For example, although the  $^{13}\text{C}$  NMR of benzene exhibits a sharp singlet at 128.7 ppm<sup>15</sup>, the signal of the tropylium ion, which contains one positive charge equally distributed over seven carbon atoms, is shifted to 155.3 ppm.<sup>15</sup> (Determination of the charge per carbon in doped  $\text{CH}_x$  is complicated by the obvious inhomogeneity of the doping. Motion of the already delocalized charge site would also lead to averaging on the NMR time scale.) We suggest that the primary contribution to the downfield shift on doping is the chemical shift arising from the removal of electrons from the  $\pi$ -system, and that any Knight shift represents a smaller contribution superimposed on this chemical shift. Moreover, since the conduction electrons in this system must be  $\pi$ -electrons, the Knight shift must involve core polarization, orbital and/or dipolar coupling; in particular both the magnitude and direction of such a shift are uncertain.<sup>16</sup>

The situation is further complicated by the current uncertainty over the interpretation of magnetic susceptibility studies on  $\text{AsF}_5$  doped polyacetylene, particularly in the intermediate doping regime ( $\sim 1-7\%$ ). Schumacher-Slichter measurements on the same 3.2% doped trans sample used in the above  $^{13}\text{C}$  NMR experiments show a low Pauli susceptibility of  $\sim 1.5 \times 10^{-7}$  emu/mole, while EPR studies on this sample yield a Pauli susceptibility of  $\sim 1 \times 10^6$  emu/mole.<sup>17</sup> Since any Knight shift should correlate with the Pauli spins, an independent resolution of the susceptibility problem will be required before a realistic estimate of the Knight shift contribution to the observed spectra can be made.

### Polypyrrole

Oxidative polymerization of pyrrole under a variety of conditions has long been known to yield a family of conducting black powders referred to collectively as the "pyrrole blacks."<sup>18</sup> The insolubility and general intractability of these materials again prohibited their straightforward characterization, although chemical degradation studies suggested a structure in which intact pyrrole rings were coupled at the  $\alpha$  positions. More recently Diaz *et al.* have developed a controlled electrochemical synthesis of this polymer, more correctly named polypyrrole, leading to flexible films with conductivities as high as  $40-100 \text{ ohm}^{-1}\text{-cm}^{-1}$ .<sup>19</sup> Unique among the conducting polymers obtained to date, polypyrrole is remarkably stable to air in its conducting form, showing only a 10% drop in conductivity after  $\sim 6$  months exposure to the atmosphere.

On the basis of electrochemical and spectroscopic data,<sup>20</sup> the polymerization of pyrrole is believed to involve coupling of the pyrrole moieties and simultaneous oxidation to yield a polymeric cation with one counterion (derived from the supporting electrolyte) for every 3-4 pyrrole rings. Under carefully controlled conditions, this oxidized pyrrole polymer can then be electrochemically reduced to form a yellow insulating polymer in its neutral state.

The characterization of polypyrrole has proved to be quite difficult; however, using CPMAS  $^{13}\text{C}$  NMR we have now been able to provide evidence which confirms structure II as the predominant form of the as-prepared conducting polypyrrole. In addition this data has provided valuable insight into possible modifications of polypyrrole which might lead to a more ordered polymer.

The relevant  $^{13}\text{C}$  NMR data are shown in Figure 6. Figure 6(a) shows the spectrum of a 17 mg sample of neutral polypyrrole film. (All sample preparation and handling was carried out under dry box conditions.) In this spectrum, three peaks can be distinguished. The major peaks are shifted  $\sim 123$  and  $\sim 105$  ppm downfield from TMS. These peaks correspond well with the  $\alpha$  and  $\beta$  carbons of the pyrrole monomer, which occur at 117 and 108 ppm downfield relative to TMS.<sup>21</sup> The two peaks confirm the presence of the pyrrole moiety in the polymer, and the downfield shift of the  $\alpha$  carbons relative to monomeric pyrrole is consistent with  $\alpha, \alpha'$  linkages.<sup>21</sup> The shoulder at  $\sim 135$  ppm may indicate the presence of some non- $\alpha, \alpha'$  linkages, e.g.,  $\alpha$ - $\beta$  linkages, although the possibility that these carbons correspond to chain end groups can not be rigorously eliminated.

Figure 6(b) shows the spectrum of a sample of the electrochemically oxidized polypyrrole perchlorate. This conducting sample was dispersed by grinding with glass powder before being loaded into the sample rotor. The spectrum shows a very broad asymmetric peak shifted downfield relative to the neutral polypyrrole, consistent with the removal of the  $\pi$  electrons and the formation of a polymeric pyrrole carbonium ion. Figure 6(c) shows the spectrum of a sample of neutral polypyrrole after oxidization with iodine vapor to give a highly conducting film. The downfield shift relative to neutral polypyrrole is greater than that of the electrochemically oxidized polypyrrole perchlorate, indicating a higher degree of oxidation consistent with the higher conductivities observed for the iodine treated samples.

Although these downfield shifts for the oxidized samples are consistent with oxidation to form carbonium ions, there may also be some contribution from a Knight shift.

#### **Poly( $\beta,\beta'$ -Dimethylpyrrole)**

The suggestion of some non- $\alpha-\alpha'$  bonding in the NMR spectrum of the parent polypyrrole led to the synthesis and polymerization of 3,4-dimethylpyrrole.<sup>22</sup> The main hope was that by eliminating the possibility for  $\alpha-\beta$  pyrrole linkage, a more ordered polymer suitable for structural studies might be obtained. This has, indeed, proved to be the case.<sup>23</sup> Poly( $\beta,\beta'$ -dimethylpyrrole) can be synthesized as a conducting film by the same electrochemical techniques used for polypyrrole. Conductivities on the order of  $10 \text{ ohm}^{-1}\text{-cm}^{-1}$  are routinely obtained.

The CPMAS  $^{13}\text{C}$  NMR spectrum of poly( $\beta,\beta'$ -dimethylpyrrole) in both neutral and conducting forms is shown in Figure 7. The most prominent difference from the spectrum of polypyrrole is, of course, the presence of the methyl carbons at  $\sim 10$  ppm. The presence of the methyl groups also causes the  $\alpha$  and  $\beta$  carbon resonances to be less well separated than in the parent polymer. Again the oxidized conducting form of the polymer shows the expected downfield shift with respect to the neutral material.

#### **CONCLUSIONS**

The above examples demonstrate the power of CPMAS  $^{13}\text{C}$  NMR spectroscopy for the analysis of the structure and reactions of polymers which are quite difficult to characterize by more conventional techniques. It is only a matter of time before this technique becomes a routine element in the characterization of organic solids.

**ACKNOWLEDGMENTS**

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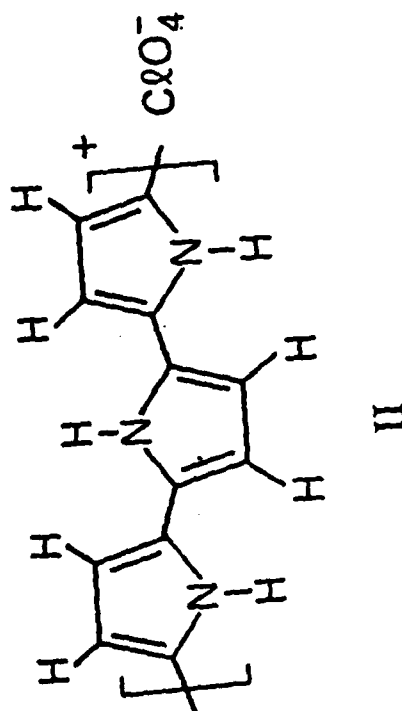


1b



1a

STRUCTURE I



STRUCTURE II

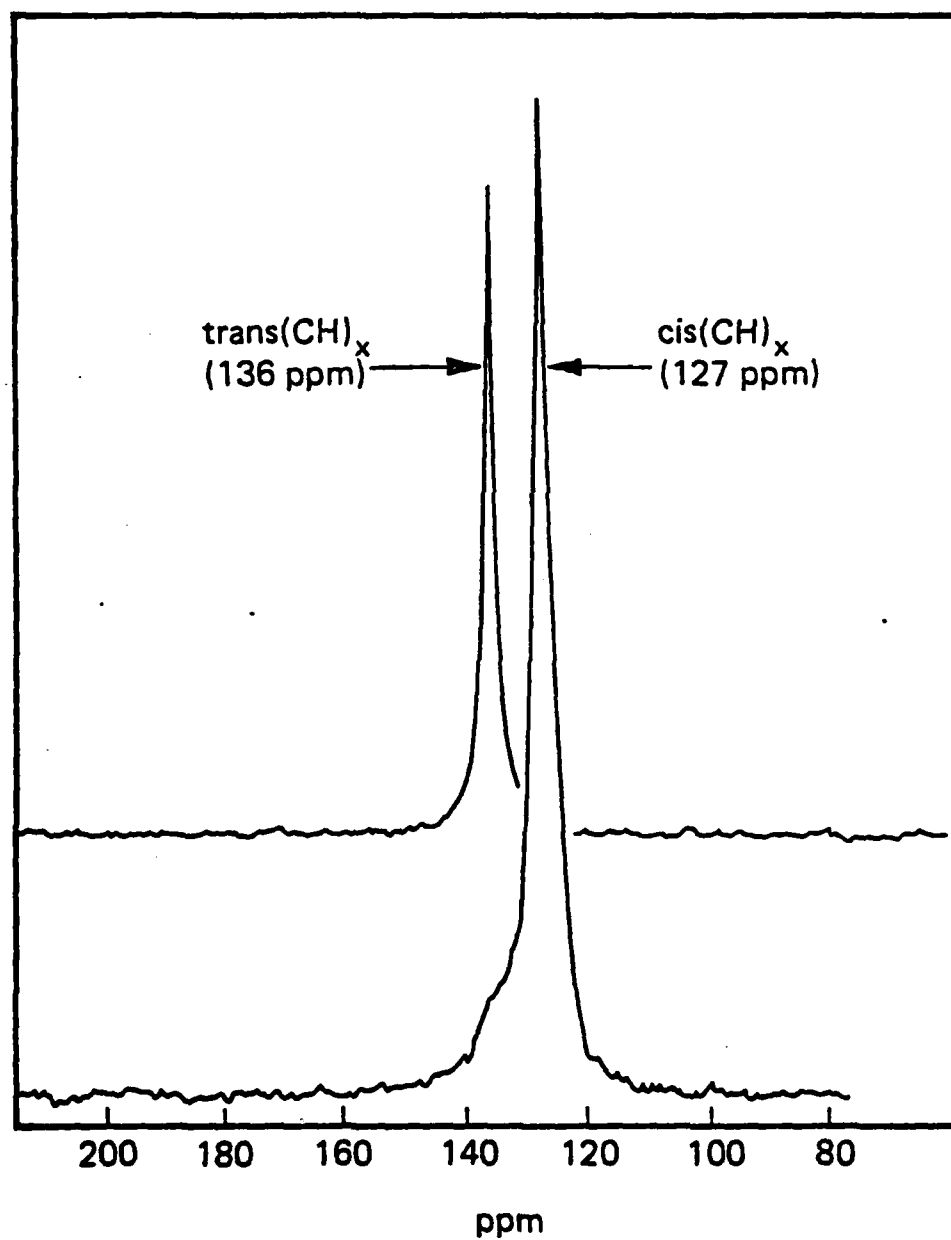


Figure 1. CPMAS  $^{13}\text{C}$  NMR spectra of pristine *cis*- and *trans*-polyacetylene.

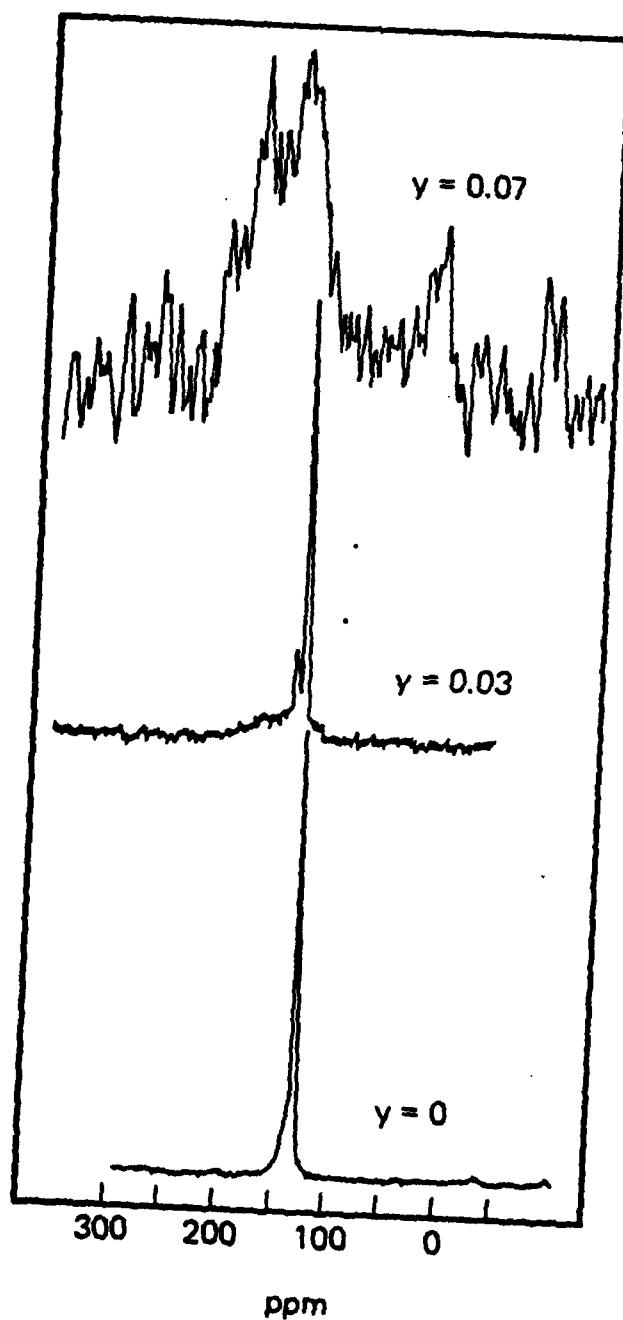


Figure 2.  $^{13}\text{C}$  NMR spectra of *cis*-polyacetylene before (bottom) and after doping with  $\text{AsF}_5$  to composition  $\text{CH}(\text{AsF}_6)_y$ .

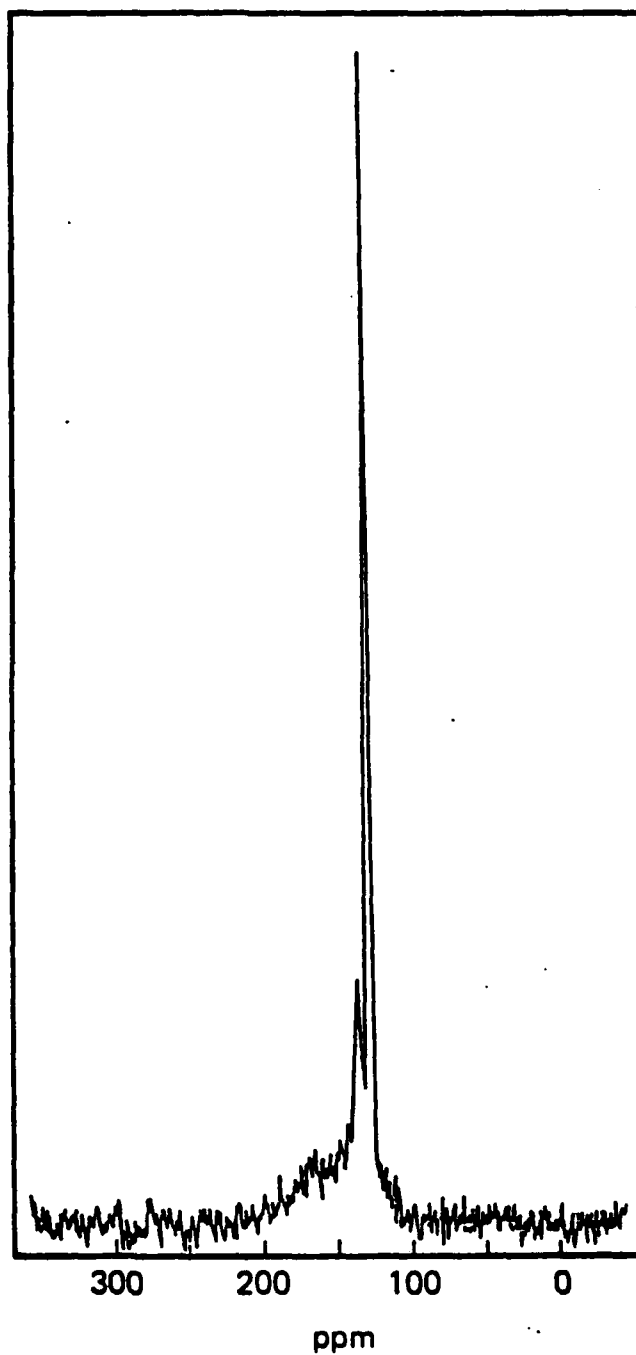


Figure 3. Expanded  $^{13}\text{C}$  NMR spectrum of  $(\text{CH}(\text{AsF}_6)_{0.03})$ .

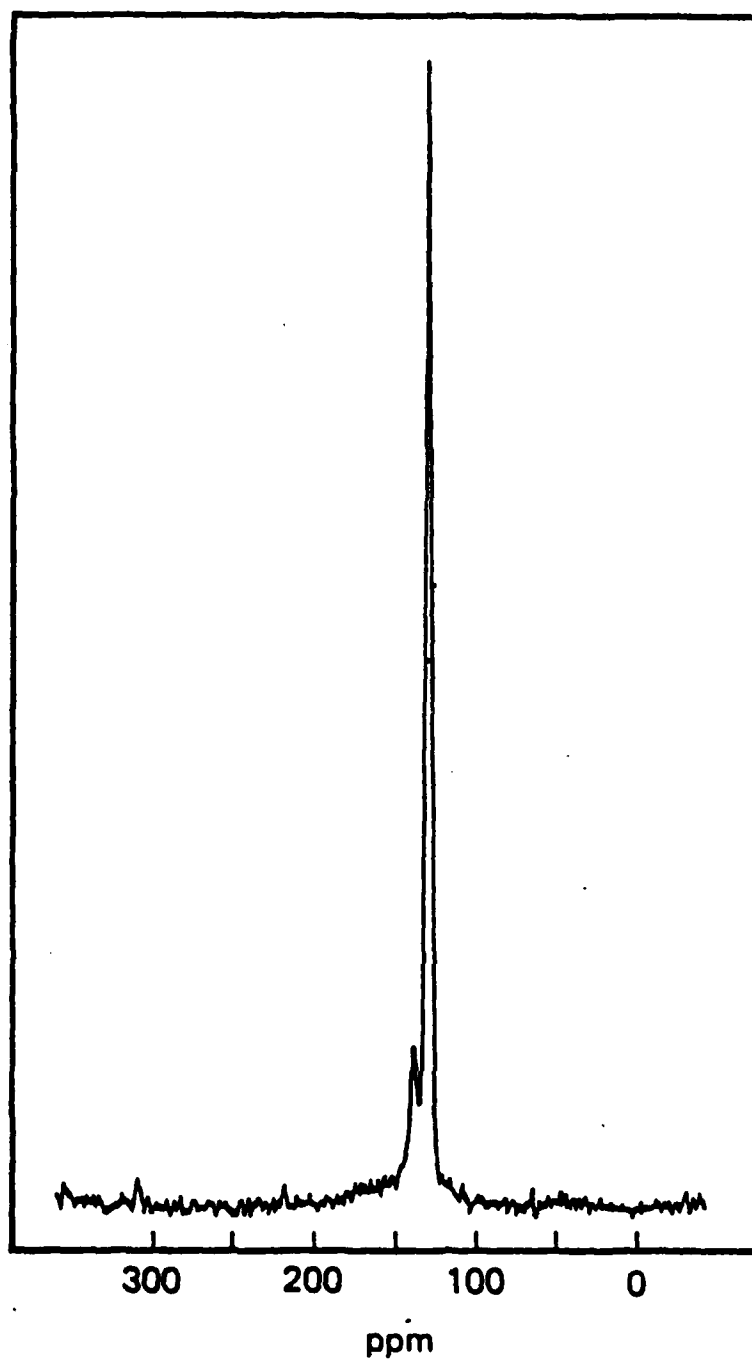


Figure 4. Expanded  $^{13}\text{C}$  NMR spectrum of  $\text{CH}(\text{AsF}_6)_{0.01}$ .



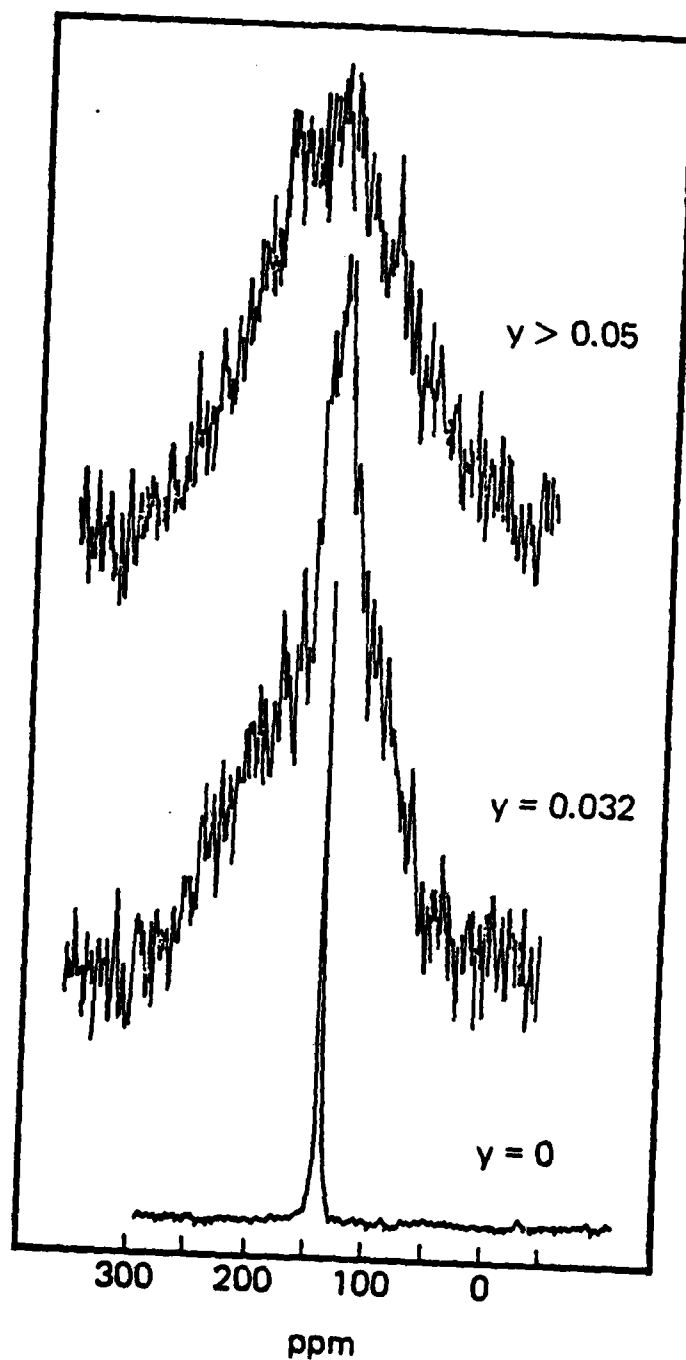


Figure 5.  $^{13}\text{C}$  NMR spectra of *trans*-polyacetylene before (bottom) and after doping with  $\text{AsF}_5$  to composition  $[\text{CH}(\text{AsF}_6)_y]$ .

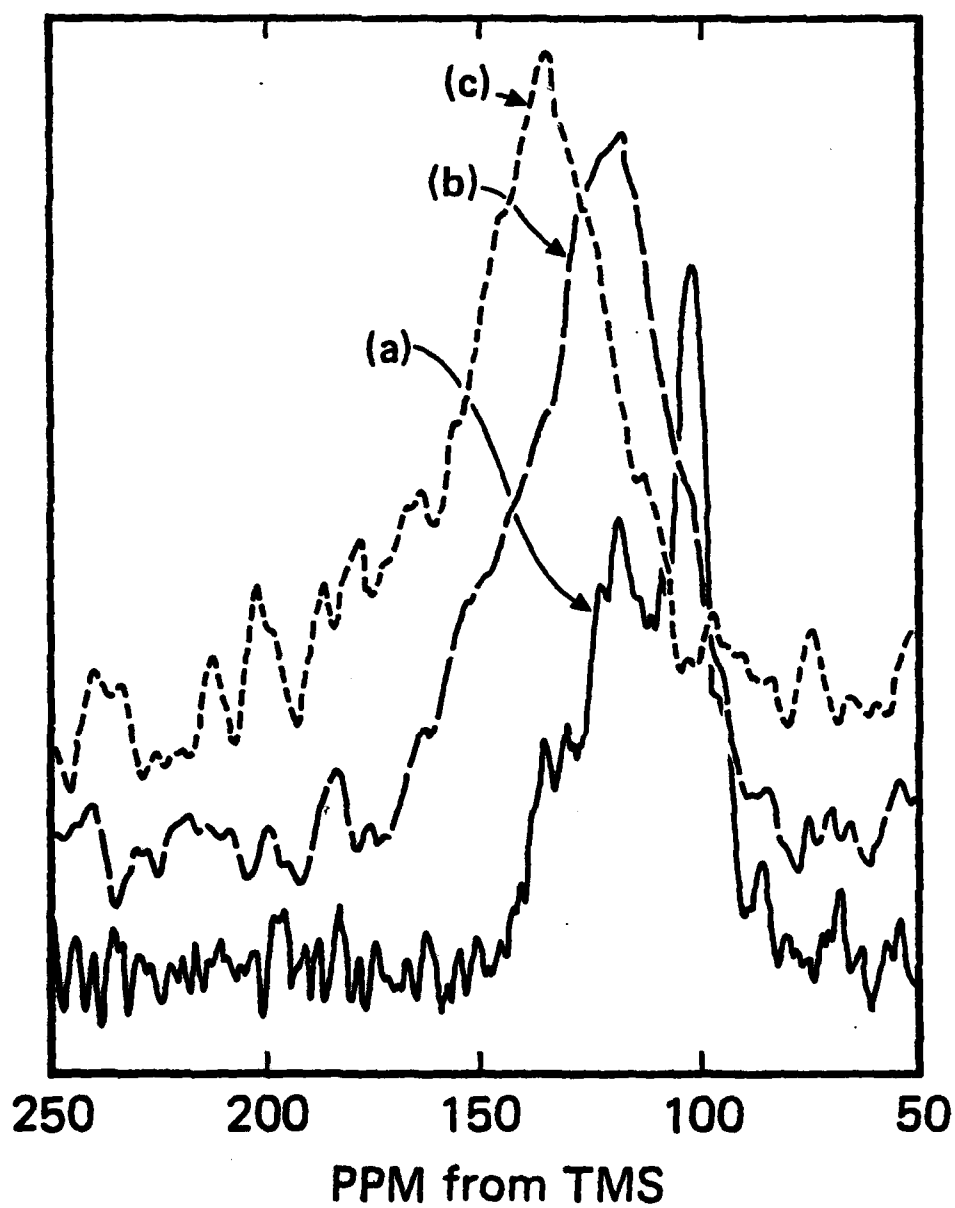


Figure 6.  $^{13}\text{C}$  NMR spectra of (a) neutral polypyrrole; (b) polypyrrole perchlorate; (c) neutral polypyrrole reacted with iodine.

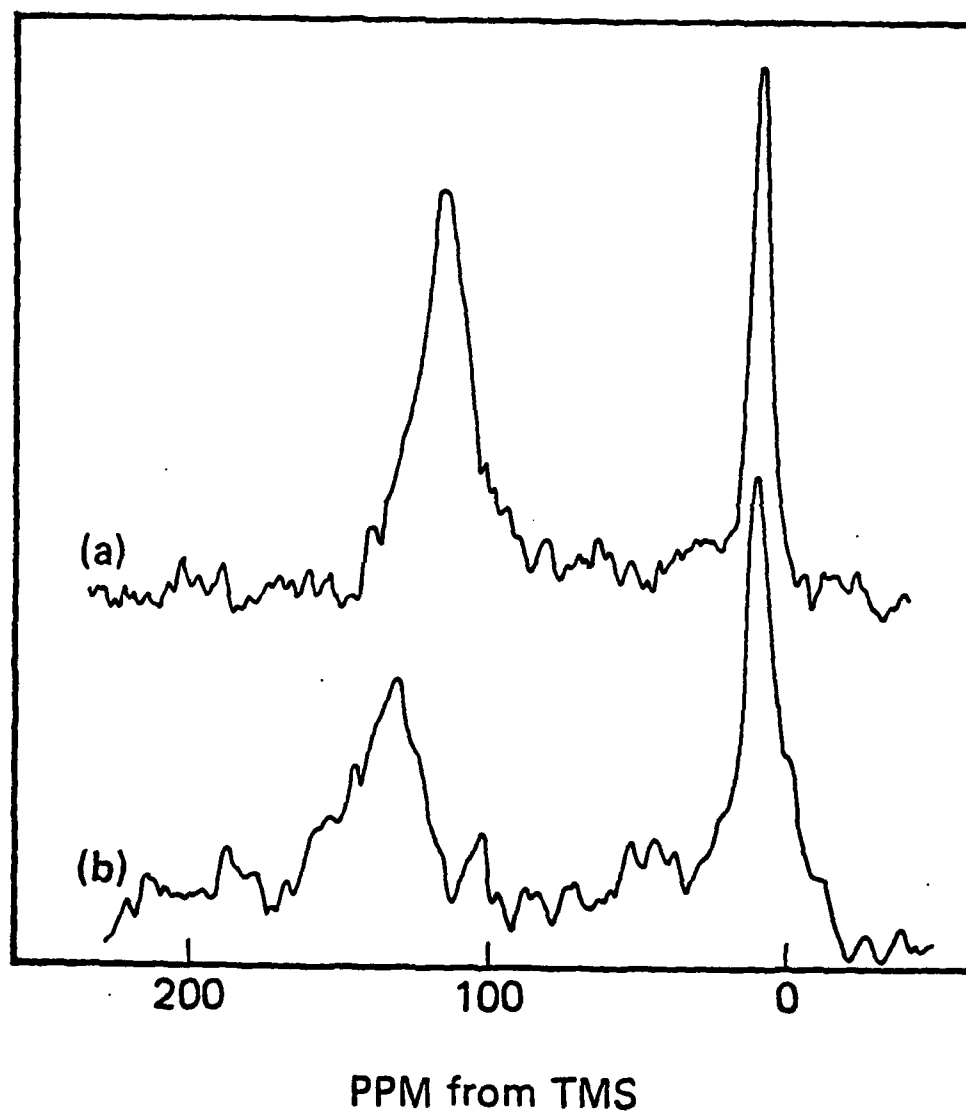


Figure 7.  $^{13}\text{C}$  NMR spectra of (a) neutral poly( $\beta,\beta'$ -dimethylpyrrole) and (b) poly( $\beta,\beta'$ -dimethylpyrrole) perchlorate.